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# PATENT ABSTRACTS OF JAPAN

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### (54) HAIR DYE COMPOSITION

#### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a hair dye composition simple to use, excellent in hair dyeing effects and fastness, scarcely damaging hair without using an oxidizing agent and without causing fouling of skin by making the composition include a direct dye and thioglycolic acid therein.

SOLUTION: This composition is obtained by including (A) a direct dye (e.g. nitro-p-phenylenediamine) and (B) thioglycolic acid and/or its salt (e.g. ammonium thioglycolate). In the composition, 0.01-10 wt.% of the ingredient A and the ingredient B in an amount of 0.005-2 wt.% expressed in terms of the thioglycolic acid are preferably contained. Furthermore, (C) 0.1-25 wt.% of a solubilizer (e.g. polyethylene glycol), (D)  $\geq 0.01$  wt.% of a thickening agent comprising an anionic polymer such as gum arabic and (E) 0.01-5 wt.% of a cationic surfactant or a cationic polymer, as necessary, are preferably contained in the composition.

#### **CLAIMS**

#### [Claim(s)]

[Claim 1] The hair dye constituent of 1 agent type characterized by containing at least one sort of direct dye, and thioglycolic acid and/or its salt.

[Claim 2] The hair dye constituent according to claim 1 characterized by direct dye

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consisting of a nitroglycerine system color.

[Claim 3] The hair dye constituent according to claim 1 to 2 characterized by being chosen out of the group which direct dye becomes from azo dye, nitroso dye, triphenylmethane dye, xanthene dye, quinoline dye, anthraquinone dye, and an indigo color.

[Claim 4] The hair dye constituent according to claim 1 to 3 characterized by including one sort chosen from the group which consists of a polyethylene glycol, a polyoxyethylene polyoxypropylene glycol, polyoxyethylene castor oil, and polyoxyethylene hydrogenated castor oil, or two sorts or more.

[Claim 5] The hair dye constituent according to claim 1 to 4 characterized by including one sort of an anionic macromolecule, or two sorts or more.

[Claim 6] The hair dye constituent according to claim 1 to 5 characterized by including one sort chosen from the group which consists of a cationic surface active agent and a cation-ized polymer, or two sorts or more.

#### DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is excellent in the hair dyeing effectiveness and robustness, and relates to the hair dye constituent of 1 agent type with little hair breakage and natural complexion dirt.

[0002]

[Description of the Prior Art] Oxidation hair dye using oxidation dye, such as a p phenylenediamine, as hair dye excels before in the hair dyeing force or robustness, and it has been widely used from a color tone being variegated. Moreover, acid dye and acid hair dye using a solvent, such as a coloring rinse and hair manicure, have also spread widely in recent years.

[0003]

[Problem(s) to be Solved by the Invention] However, oxidation hair dye needs to oxidize and needs to make a color color, and in 1 agent type oxidation hair dye which uses the oxygen in air as an oxidizer, since sufficient oxidizing power is not obtained but the hair dyeing force becomes weak, 2 agent types which use, mixing with oxidizers, such as a hydrogen peroxide, are general. Therefore, there are problems, such as breakage on the hair by oxidizers, such as a hydrogen peroxide, and a stimulus to the skin.

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[0004] moreover, warming complicated at the time of hair dyeing in blending a color with high concentration in order to use acid hair dye in an acid field, and not to use an oxidizer and to acquire but sufficient hair dyeing effectiveness that hair breakage is comparatively slight — actuation is needed. Furthermore, if drugs adhere to the scalp or the skin, it will be dyed easily, and there is a fault that considerable period dirt will remain. Moreover, in order to raise the aesthetic property of a result, when the cationic surface active agent, the cation-ized macromolecule, etc. were blended, in order to form acid dye and complex, lowering of the hair dyeing force was remarkable, and utilization was difficult. Furthermore, although 2 agent type hair dye which consists of the 1st agent which used a nitroglycerine system color and alkali chemicals as the principal component, and the 2nd agent which used the hydrogen peroxide as the principal component is also known, since [ that the hair dyeing force is weak ] robustness is also bad, it has not spread.

[0005] Thus, it excelled in the hair dyeing effectiveness and robustness, and the hair dye constituent of 1 agent type with little hair breakage and natural complexion dirt was not yet obtained, but development of this hair dye constituent was desired.
[0006]

[Means for Solving the Problem] As a result of repeating research wholeheartedly that the above-mentioned trouble should be solved, by combining direct dye, thioglycolic acid, and/or its salt, not using the oxidizer, this invention person was simple, excellent in the hair dyeing effectiveness and robustness, there was little hair breakage, found out not causing natural complexion dirt further, and resulted in this invention.

[0007] That is, this invention can be used simple, is excellent in the hair dyeing effectiveness and robustness, and offers the hair dye constituent of 1 agent type with little hair breakage and natural complexion dirt.

[0008] Hereafter, this invention is explained to a detail.

[0009] what has tar system coloring matter, natural coloring matter, etc. well-known as direct dye used for the hair dye constituent of this invention — it can be used — one sort — or two or more sorts may be used together. Also in it, a nitroglycerine system color, azo dye, nitroso dye, triphenylmethane dye, xanthene dye, quinoline dye, anthraquinone dye, or an indigo color can acquire the good hair dyeing effectiveness, and is desirable, and especially a nitroglycerine system color is desirable from the point of the hair dyeing effectiveness. Moreover, it is desirable still more desirable to blend 0.01 to 10% of the weight into a hair dye constituent, and these colors are 0.05 - 5 % of the weight. When fewer than 0.01 % of the weight, the hair dyeing effectiveness is

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inadequate, and when [than 10 % of the weight] more [conversely], it becomes remarkable and is not desirable [the effectiveness / dyeing to about / that the hair dyeing force does not improve /, the scalp and a finger].

[0010] As an example of direct dye, a nitro p phenylenediamine, a PARANITORO alt.phenylenediamine, A PARANITORO meta-phenylenediamine, a 2-amino-4-nitrophenol, A 2-amino-5-nitrophenol, picramic-acid, N1 and N4, and N4-tris (2-hydroxyethyl)-2-nitro p phenylenediamine, 4-[(2-nitrophenyl) amino] phenol, an N1-(2-hydroxyethyl)-2-nitro p phenylenediamine, 2 and 2'-[(4-amino-3-nitrophenyl) imino] bis-ethanol, An N-(2-hydroxyethyl)-2-nitroaniline, 2-[[2-(2-hydroxy ethoxy)-4-nitrophenyl] amino] ethanol, An N1-(2-hydroxyethyl)-4-nitro alt, phenylenediamine, Those salts and "Ministerial Ordinance by which the tar dye which can be used for drugs etc. is provided" (a notification in Showa 41) Nitroglycerine system colors of the yellow No. 403 among the colors (it abbreviates to a certified color hereafter) defined by the Ministry of Health and Welfare, such as (1), Similarly A certified color, red No. 2, red No. 102, red No. 201, red No. 225, Red No. 227, red No. 501, red No. 502, red No. 503, red No. 504, Red No. 505, red No. 506, orange No. 205, orange No. 402, Orange No. 403, yellow No. 4, yellow No. 5, yellow No. 402, yellow No. 404, Azo dye, such as yellow No. 405, yellow No. 406, yellow No. 407, \*\*\*\*\* No. 201, and black No. 401, the same - nitroso dye, such as green No. 401, - blue No. 1 and blue No. 202 similarly Triphenylmethane dye, such as blue No. 203, blue No. 205, green No. 3, green No. 205, and green No. 402, Similarly (1), (1) of red No. 105, red No. 106 of red No. 3 and red No. 104, (2), red No. 231 of (1) and red No. 230 of red No. 218 and red No. 230, Red No. 232, red No. 401, orange No. 201, orange No. 207, The xanthene dye of (1) and yellow No. 202 of yellow No. 201 and yellow No. 202, such as (2), Similarly Quinoline dye, such as yellow No. 203 and yellow No. 204, 1-amino-4-methylamino anthraquinone, 1,4-diaminoanthraquinone, the certified color blue No. 403, green No. 201, green No. 202, purple No. 201, the anthraquinone dye of a purple No. 401 grade, the indigo color that are similarly blue No. 2, blue No. 201, etc. are mentioned.

[0011] The action mechanism of this invention softens hair in reduction with a mercapto compound, and raises the permeability to the hair of a color, and it is thought that it is what promotes dyeing. Although thioglycolic acid, cysteines, thiourea, etc. are mentioned as a mercapto compound, thioglycolic acid of effectiveness is the highest. As the thioglycolic acid used for the hair dye constituent of this invention, and its salt, thioglycolic acid, thioglycolic acid ammonium, thioglycolic acid monoethanolamine, sodium thioglycolate, calcium thioglycollate, etc. are mentioned. The loadings are 0.01



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1 % of the weight still more preferably 0.005 to 2% of the weight as thioglycolic acid. Sufficient dyeing facilitatory effect is not acquired, and although it is enough, it becomes hair breakage and the cause which produces a wave down with Parma operating hair further and is not desirable [ a dyeing facilitatory effect ], when [ than 2 % of the weight ] more, when there is less concentration of thioglycolic acid than 0.005 % of the weight in order to return the keratin protein in hair superfluously. [0012] In the hair dye constituent of this invention, since poorly soluble direct dye may be blended with water, a solubilizing agent is contained suitably. Since a solvent or a surfactant is used for a solubilizing agent, the hair dyeing effectiveness may be checked depending on the case. In this invention, when a polyethylene glycol, a polyoxyethylene polyoxypropylene glycol, polyoxyethylene castor oil, polyoxyethylene hydrogenated castor oil, etc. were blended, while it was rare to check the hair dyeing effectiveness and it promoted the hair dyeing effectiveness depending on the class of color, it found out that a color could be solubilized. As loadings, it is desirable to blend 0.1 to 25% of the weight into the hair dye constituent of this invention. It is 1 - 10 % of the weight still more preferably. When fewer than 0.1 % of the weight, possibility of the capacity which solubilizes a color being too low and sufficient hair dyeing force not being acquired, and checking the hair dyeing effectiveness when [ an 25 % of the f weight ] f more f becomeslarge.

[0013] The hair dye constituent of this invention can be made into pharmaceutical forms, such as the shape of liquid, a milk liquid, and a cream, gel, the shape of a paste, and aerosol form. However, since this invention is the hair dye constituent of 1 agent type, moderate viscosity is required in order to prevent a liquid lappet and spilling. Although definition is not received especially in the class of thickener when making drugs thicken using a thickener, the stability of a viscous constituent to an anionic macromolecule is the most desirable.

[0014] As an anionic giant molecule, a carboxyvinyl polymer, polyacrylic acid, its salt, etc. are mentioned to gum arabic, xanthan gum, tragacanth gum, a carrageenan, carboxymethylcellulose sodium, and a list.

[0015] The loadings are 0.01 % of the weight or more, and can be adjusted to suitable viscosity.

[0016] When the cationic surface active agent or the cation-ized polymer was blended with the hair dye constituent of this invention, it also found out collectively that change of the hair color tone after hair dyeing decreased that the smoothness as the finger at the time of a rinse and the aesthetic property of a result become very good especially,

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and moreover at the time of a shampoo. As a cationic surface active agent, for example Chlorination alkyl trimethylammonium, Chlorination lauryl trimethylammonium, chlorination cetyl trimethylammonium, A cetyltrimethylammonium bromide, stearyl chloride trimethylammonium, bromination — stearyl trimethylammonium and lauryl bromide trimethylammonium — Chlorination dialkyl dimethylannmonium, chlorination dicetyl dimethyl ammonium, Chlorination distearyldimethylbenzylammonium, chlorination JIKOKOIRU dimethylannmonium, Alkyl ammonium salt, alkyl benzyl ammonium salt, etc., such as chlorination millimeter still dimethylbenzyl ammonium and stearyldimethylbenzylammonium chloride [ whether as a cation-ized polymer, it combines with a polymer chain and the amino group or ammonium is included, and ] Or dimethyl diaryl ammonium halide is included as a configuration unit at least. For example, a cation-ized cellulosic, cationic starch, a cation-ized Cyamoposis Gum derivative, a cation-ized hydrolysis keratin, a cation-ized dextran, diaryl quarternary ammonium salt / acrylamide copolymerization object, the 4th class-ized polyvinyl-pyrrolidone derivative, etc. are mentioned.

[0017] If the loadings have 0.01 · 5 desirable % of the weight and there is than 0.01 % of the weight, the aesthetic property of good hair is not obtained and they cannot expect sufficient effectiveness for prevention of the color tone change after hair dyeing. [less] The effectiveness changes and is not economical even if it exceeds 5 % of the weight. [0018] Furthermore, in the range which does not bar the effectiveness of this invention, addition combination of the well-known component can be carried out conventionally at the hair dye constituent of this invention. For example, a higher-alcohol, liquid paraffin, ester-oil, fatty-acid, silicone and its derivative, vaseline, polyhydric-alcohol, ultraviolet ray absorbent, antiseptics, surfactant, pH regulator, alkali-chemicals, perfume, and pearl-ized agent etc. is mentioned.

[0019] Moreover, the hair dye constituent of this invention shows the best hair dyeing force and robustness in the specific pH field 6·11, i.e., pH. However, when safeties, such as a stimulus, are taken into consideration to the scalp, adjusting to ten or less pH is desirable.

[0020]

[Embodiment of the Invention] Next, although an example is given and this invention is explained concretely, this invention is not limited to description of the following examples, unless the summary is exceeded.

[0021]

[Example]

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Example 1 Weight % blue No. 1 0.5 Thioglycolic acid ammonium 0.5 Monoethanolamine 2.0 Carboxyvinyl polymer 1.5 Purified water \*\* Amount [0022]

Example 2 A weight % nitro p phenylenediamine 1.5 Thioglycolic acid monoethanolamine 1.0 Polyethylene glycol 1500 5.0 Monoethanolamine 1.0 Xanthan gum 2.0 Hydroxyethyl cellulose hydroxypropyl Trimethyl ammoniumchloride ether 0.5 Purified water \*\* Amount [0023]

Example 3 Weight % 1,4-diaminoanthraquinone 1.5 Thioglycolic acid monoethanolamine 1.0 Polyoxyethylene hydrogenated castor oil 8.0 Monoethanolamine 1.0 Sodium polyacrylate 2.0 Purified water \*\* Amount [0024]

Example 4 The weight % red No. 213 1.0 Thioglycolic acid ammonium 1.0 Polyethylene glycol 400 10.0 28% aqueous ammonia 3.0 Olive oil 5.0 Polyoxyethylene (15) cetyl ether 5.0 Sodium polyacrylate 0.5 Stearyl chloride trimethylammonium 3.0 Stearyl alcohol 10.0 Purified water \*\* Amount [0025]

Example 1 of a comparison Weight % blue No. 1 0.5 Monoethanolamine 2.0 Carboxyvinyl polymer 1.5 Purified water \*\* Amount [0026]

Example 2 of a comparison The weight % blue No. 1 0.5 Benzyl alcohol 5.0 Ethyl alcohol 10.0 Citric acid 0.5 Carboxyvinyl polymer 3.0 Purified water \*\* Amount [0027] Example 3 of a comparison The weight % red No. 213 1.0 Polyethylene glycol 400 10.0 Benzyl alcohol 5.0 Citric acid 0.5 Olive oil 5.0 polyoxyethylene (15) cetyl ether 5.0 Stearyl alcohol 10.0 Purified water \*\* Amount [0028]

The example 4 (2 agent types) of a comparison

(The 1st agent) A weight % nitro p phenylenediamine 1.5 Thioglycolic acid ammonium 1.0 Polyethylene glycol 400 10.0 28% aqueous ammonia 3.0 Olive oil 5.0

Polyoxyethylene (15) cetyl ether 5.0 Stearyl chloride trimethylammonium 3.0 Stearyl alcohol 10.0 Purified water \*\* Amount (the 2nd agent) The weight % polyoxyethylene (4) nonylphenyl ether 5.0 Polyoxyethylene (9) nonylphenyl ether 5.0 Hydrogen peroxide (35%) 17.0 Cetanol 3.0 Purified water \*\* They are 1 agent and 2 agents at the time of an amount activity. Tales doses mixing is carried out and it applies.

[0029] The examples 1-4 and the examples 1-4 of a comparison which are shown above were adjusted, hair dyeing trial, robustness trial, skin dyeing property trial, and breakage on hair were evaluated, and the result was shown in a table 1.

[0030] (1) The hair dyeing trial crest wool bundle (white; weight of about 2g) was washed using 5g of 5 % of the weight water solutions of sodium lauryl sulfate, and it rinsed enough with warm water. After wiping off moisture excessive after that and applying 2g of hair dye constituents of examples 1-4 and the examples 1-3 of a

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comparison, it was left for 30 minutes in the thermostat (37 degrees C). About the example 4 of a comparison, tales-doses mixing of 1 agent and the 2 agents was carried out, and hair dyeing was carried out on these conditions. Subsequently, it rinsed and dried and the following criteria estimated the hair after hair dyeing.

- O -- The hair dyeing force is fitness (it colors uniformly and deeply and white is not conspicuous) very much.
- O ·· The hair dyeing force is fitness (it is colored homogeneity and white is not conspicuous).
- \*\* -- The hair dyeing force is imperfection (a stain ball is uneven and white is a little conspicuous).
- x ·· The hair dyeing force is very bad (a stain ball is uneven and white is conspicuous). [0031] (2) It was immersed in the sodium lauryl sulfate water solution for 20 minutes 1 50 degree C% of the weight one day after the trial of the hair bundle which carried out hair dyeing by the robustness trial hair dyeing trial, and washout desiccation was enough carried out with warm water after that. Extent of fading in this case was evaluated as compared with the hair dyeing hair bundle before a robustness trial. O most ·· decoloring ·· there is nothing ·· a fading emergency ·· fitness O·· decoloring ·· few ·· fading fitness \*\*·· decoloring and \*\* ·· large ·· fading and \*\* poor x·· decoloring ·· large ·· poor fading [0032] (3) Leave it for 30 minutes after applying to the magnitude of a ball 0.5g (it is the tales doses mixture of 1 agent and 2 agents about the example 4 of a comparison) of hair dye constituents of 10 yen previously adjusted to the skin dyeing property trial Homo sapiens forearm inside section. Subsequently, after rinsing, the dyeing section was lightly ground against the absorbent cotton into which the soap solution was made to soak about 20 times, and it measured and estimated again extent of the color dyed on the skin after rinsing.
- O ·· [·· It dyes on the skin and is poor color remaining \*\*\*\*.] Most color remainder cannot be found in the skin and it is very fitness O. ·· It is fitness \*\*, without being conspicuous although slightly dyed on the skin. ·· It dyes on the skin and they are the color remainder, \*\*\*\*\*\*\*, and \*\* poor x. [0033] (4) The hair front face before and after breakage hair dyeing processing of hair was observed with the electron microscope (one 3000 times the scale factor of this), the following criteria estimated extent of breakage on the cuticula pili, and assessment which was was made into representation.
- O ·· Breakage is not accepted by hair dyeing.
- O ·· The breakage on slight upheaval, a crack, exfoliation, etc. is accepted in the cuticula pili.



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\*\* · · The breakage on slight upheaval, a crack, exfoliation, etc. is accepted in the cuticula pili.

x · The breakage on serious upheaval, a crack, exfoliation, etc. is accepted in the cuticula pili.

[0034]

[A table 1]

	実 施 例				比較例			
	1	2	3	4	1	2	3	4
染 毛 効 果	0	0	0	0	×	0	Δ	0
堅 牢 性	0	. 🔿	. 🔘	0	×	0	0	Δ
皮膚染着性	0	0	0	٥	0	×	×	0
毛髪の損傷	0	0	0	0	0	0	0	×
総合評価	0	0	0	0	×	Δ	Δ	Δ

## [0035]

[Effect of the Invention] The hair dye constituent of this invention does not have the stimulus by the oxidizer, is excellent in the hair dyeing effectiveness and robustness, and offers a hair dye constituent with little dirt of hair breakage, the scalp, or the skin.

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